

*Gill JPF SM*  
National Aeronautics and Space Administration  
Goddard Space Flight Center  
Contract No. NAS-5-3760

ST-AM-RWP-10423

ON THE MICROWAVE ABSORPTION SPECTRUM OF  
MOLECULAR OXYGEN

by  
A. P. Naumov

(USSR)

GPO PRICE \$ \_\_\_\_\_

CFSTI PRICE(S) \$ \_\_\_\_\_

Hard copy (HC) .70

Microfiche (MF) .50

ff 653 July 65

N 67 12917

FACILITY FORM 602	(ACCESSION NUMBER)	(THRU)
	11	1
	(PAGES)	(CODE)
	CR-80152	13
	(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

8 December 1965

ON THE MICROWAVE ABSORPTION SPECTRUM  
OF MOLECULAR OXYGEN\*

IVUZ. Radiofizika  
Tom 8, No. 4, 668 - 678,  
Izd. Gor'kovskogo Universiteta  
GOR'KIY, 1965

by A. P. Naumov

SUMMARY 12917

An inconsistency is noted in the Maryott-Birnbaum hypothesis about the resonance frequency shift of the microwave spectrum of oxygen absorption for pressures of several atmospheres. It is shown that the approximate accounting for the nonresonance absorption of  $O_2$  is sufficient for the quantitative explanation of the results of measurements of micro-radiowave absorption at high pressures. The description of the oxygen absorption spectrum in the 5 mm band may be obtained by the standard method for pressures  $P = 7 \pm 8$  atm.

*Author*

The question of centimeter and millimeter radiowave absorption by oxygen molecules at increased pressures of the order of several atmospheres was lately discussed on several occasions [1 - 4] (see also the review [5]). The experimental and theoretical results of the works [1 - 3] allow to obtain additional information on the spectrum of atmospheric oxygen (nonresonance absorption, dependence of the width of oxygen lines on pressure), which in its turn is prerequisite for making more precise the characteristics of microwave propagation, for the solution of certain geophysical problems, and so forth. We should like, however, to draw attention to the uncertainty of the interpretation of the respective experimental results presented in [1, 3, 4]. It is referred here to the hypothetical assertion by Mayriott-Birnbaum [1] of resonance shift of oxygen triplets  $\nu_{K\pm}(P)$  at pressure increase, which received a quantitative treatment in [3]. An attempt to substantiate this hypothesis theoretically has been made in the work [4].

\* О МИЛЛИМЕТРОВОМ СПЕКТРЕ ПОГЛОЩЕНИЯ МОЛЕКУЛЫ АЗОТА.

According to the opinion of the authors of [3], there takes place for the oxygen spectrum at pressure  $P$  the correlation

$$\nu_{K\pm}(P) = \nu_{K\pm}^0 - aP, \quad (1)$$

where  $\nu_{K\pm}^0$  is the resonance frequency at low pressure ( $P \approx 2 + 10$  mm Hg)  $a = 0.4$  Mc/mm Hg. It follows from the expression (1) that for  $P = 760$  mm Hg  $\nu_{K\pm}(P) - \nu_{K\pm}^0 = 0.3$  g cps, that is, in the resonance region  $\nu_{K\pm}^0 \approx 60$  g cps, the shift of resonance frequencies constitutes, according to [3], nearly 0.5% even at standard atmospheric conditions. Such a low departure of resonance frequencies of oxygen transitions from the usually admitted requires nonetheless a substantial reviewing of a series of data on the oxygen absorption spectrum. In particular, the half-widths of atmospheric oxygen's spectral lines, which cannot be measured directly at sea level because of line overlapping and are found only from the comparison of the experimental absorption coefficient in the resonance region with the calculated one, will differ in the presence of the shift  $\nu_{K\pm}^0$  by about 30%, while the equivalent path lengths of radiowaves in the terrestrial atmosphere in  $\lambda \approx 5$  mm wavelengths will depart from the values found in [9, 30] by 30 + 40 percent.

1. - We shall briefly discuss the arguments, which lead the authors of [1, 3, 4] to the corroboration of the shift of  $O_2$  resonance frequencies.

a) The excess of measured radiowave absorption in oxygen at  $P > 10$  atm and at frequencies  $\nu = 9.07$  g cps and  $23.34$  g cps from the computed absorption [6] served in [1] as such an argument. An attempt [1] to "improve" the computed values of the absorption coefficient [6] by decreasing those of  $\nu_{K\pm}^0$  met with objections already in [2], where it was shown by the perturbation method that the matrix elements of the energetic states of the molecule  $O_2$ , and consequently the resonance frequencies  $\nu_{K\pm}^0$  too do not vary to any notable extent at pressure increase. It was also found in [2] that the matrix elements of transitions  $K + 1 \leftrightarrow K - 1$  become different from zero at  $P > 10$  atm and the respective quantum transitions condition in the spectral region studied by Mayriott-Birnbaum a higher radiowave absorption [1].

b) Authors of [3] measured the absorption in a series of frequencies in the range  $\nu = 48 + 70$  g.cps at pressures  $P = 0 + 14$  atm. This

band lies in the oxygen absorption maximum and the transitions  $K + 1 \leftarrow \rightarrow K - 1$  do not contribute to this region. It was found that the values of the absorption coefficients of  $O_2$ , theoretical as well as experimental, are in a satisfactory agreement, provided we estimate the condition (1) as fulfilled (nowhere did the discrepancies of calculations exceed 15% relative to experimental data). In [3] the absorption coefficient was computed by the formula

$$\gamma = c^2 v^2 P \sum_K \frac{\gamma_{K\pm} (\Delta\nu_{K\pm}/P)}{(\nu_{K\pm}^0 - aP)^2} \frac{\delta\nu}{(\nu - \nu_{K\pm}^0 + aP)^2 + (\delta\nu)^2}, \quad (2)$$

where  $\gamma_{K\pm}$  and  $\Delta\nu_{K\pm}$  are respectively the intensity and the half-width of the spectral line at low pressure,  $\delta\nu$  is the half-width of the line at pressure  $P$ ,  $\nu$  and  $\bar{\nu}$  are respectively the outer field frequency in  $\text{cm}^{-1}$  and in g.cps,  $c$  is the speed of light.

Formula (2) has been obtained in the following assumptions:

1) the shape of the spectral line is described by the Van Vleck-Weisskopf expressions [12], the term  $\delta\nu[(\nu + \nu_{K\pm}^0 - aP)^2 + (\delta\nu)^2]^{-1}$  being at the time neglected by comparison with the term  $\delta\nu[(\nu - \nu_{K\pm}^0 + aP)^2 + (\delta\nu)^2]^{-1}$ ;

2) it is estimated that nonresonance absorption of  $O_2$  is negligibly small by comparison with the resonance absorption in the entire band  $\nu = 49 \leftarrow 70$  g.cps.

Even if we accept the viewpoint of the authors of [3], the error in formula (2) is still easy to detect. In reality, following the deduction in [6], of the formula for the absorption coefficient of  $O_2$ , and estimating that at low pressure  $P_1$  we have (when the contribution of all lines besides the considered one can be neglected)

$$\gamma_{\text{pes}} = \gamma_{K\pm} = AT^{-3} (\nu_{K\pm}^0)^2 \mu_{K\pm}^2 e^{-BhcK(K+1)/kT} \frac{1}{\Delta\nu_{K\pm}/P_1} \quad (3)$$

(the rotational constant of the oxygen molecule  $B = 1.44 \text{ cm}^{-1}$ ,  $k$  is the Boltzmann constant), we shall finally have

$$\gamma = c^2 v^2 P \sum_K \frac{\gamma_{K\pm} (\Delta\nu_{K\pm}/P_1)}{(\nu_{K\pm}^0)^2} \frac{\delta\nu}{(\nu - \nu_{K\pm}^0 + aP)^2 + (\delta\nu)^2}. \quad (4)$$

The difference in formulas (2) and (4) is of little effect in the resonance itself, but it is significant at the extremities of the band 48 - 70 g.cps. Thus, if the calculation by formula (2) in the frequencies  $\nu = 48.9$  g. cps and 68.7 g. cps leads to discrepancies with the experiment of [3], by, say 2 - 3 %, the analogous comparison with the calculated value of  $\gamma$  by the formula (4) will already give a departure of nearly 16%.

c) The shift of resonance frequencies of  $O_2$  in [4] is interpreted with the aid of the theory of adiabatic collisions (quantitative estimates of the values of  $a$  in the theory brought out in [4] are absent). But it is well known (see for example #7, ch. 13 in [16]), that in the microwave band the latter have no significant value, for the interaction energy between colliding molecules, necessary for a notable phase variations of the oscillating molecule (characteristic of adiabatic collision), is greater than is required for the transition between the ground and the excited states. Moreover, the kinetic energy of molecules is sufficiently great at standard temperatures ( $kT > h\nu$ ). The latter is one of the conditions of existence of transitions at collisions, that is, it constitutes evidence of the obvious predomination of adiabatic collisions in the microwave band, which do not lead to any shift of resonance frequency.

Evidently, the above-said does not exclude a certain effect of adiabatic collisions upon the microwave spectrum; these take place at any rate and induce small shifts of resonance frequencies  $\nu_{K\pm}^0$ . But spectroscopic data (see for example [16]) lead to the following estimates:  $|\nu_{K\pm}(P) - \nu_{K\pm}^0| < 0.05 \delta\nu$ ; for the pure oxygen, utilizing the usual writing of [9]  $\delta\nu = [a_{K\pm}(P)]_{cp} P$ , we have  $a/[a_{K\pm}]_{cp} < 0.05$ . It is easy to ascertain that the last correlation is already no longer fulfilled for the spectrum of oxygen if we use the value  $a = 0.4$  Mc / mm Hg proposed by the authors of [3] and the value  $(a_{K\pm})_{cp} = 1.17$  Mc / mm Hg proposed by the authors of [9].

As to the inversion spectrum of ammonium, of which analogy with the above is introduced by the authors of [1, 3] and for which the pressures  $p \approx 1 + 2$  atm, a notable resonance frequency decrease is observed, the cause of the shift consists here in the characteristic of interaction of molecules having such a configuration. Consideration of wave functions of  $NH_3$  perturbation confirms the possibility of inversion frequencies shift.

But the example noted has no relationship of any kind with the microwave spectrum of oxygen.

Drawing a balance sheet of the brief critical review of the works [1 - 4], it is possible to conclude that the hypothesis of oxygen resonance frequencies shift, at pressure increase, did not receive a theoretical confirmation (see [2]), and its only source is in the non-correspondence of the Van Vleck theory [6] with the experimental results of [1, 3]. Amongst the latter references the greater interest is offered by those of [3] at  $P < \text{atm}$ , obtained in the resonance region, where the shift of frequencies  $\nu_{K\pm}$  is most significant for the value of absorption, so long as it actually takes place. Moreover, the transitions  $K + 1 \leftarrow \rightarrow K - 1$ , resolved at high pressures, do not contribute to absorption in that region and they do not distort the spectrum of  $O_2$ .

2.- The first thing that imposes itself in the way of interpreting the measurements of [3] is the elimination of the defect inherent to the shape of the Van Vleck-Weisskopf line which was utilized in the computations of [1, 3]. This defect consists in that the absorption maximum for each line, computed by the formula (2) at  $a = 0$ , takes place in the frequency  $\nu_m = \nu_{K\pm}^0 + (\Delta\nu_{K\pm})^2/\nu_{K\pm}^0$  and not  $\nu_{K\pm}^0$ . It is easy to convince oneself of that by evaluating with the aid of formula (2) the equality  $d\gamma/d\nu = 0$ . The circumstance noted does not affect the spectrum of  $O_2$  at all under standard atmospheric conditions, so that the corresponding shift of resonance frequency is equal to 0.0006 g. cps and the term  $(\Delta\nu_{K\pm})^2/\nu_{K\pm}^0$  constitutes only 0.01% of the value of  $\nu_{K\pm}^0$ . However, at pressure  $P \approx 10 \text{ atm}$ , the term  $(\Delta\nu_{K\pm})^2/\nu_{K\pm}^0$  is already equal to 1.4 g. cps, which notably displaces the theoretical absorption curve toward the side of high frequencies. At substitution in (2) of  $\nu_{K\pm}^0$  by  $\nu_{K\pm}^0 - (\Delta\nu_{K\pm})^2/\nu_{K\pm}^0$  (it is estimated that  $a = 0$ ) the computed absorption coefficient corresponds better to experimental data of [3] than without taking into account the correction, but quantitatively this improvement is insufficient for the complete interpretation of measurements of [3]\*\*.

---

\* The shape of the spectral line obtained from the solution of the kinetic equation [14] gives the absorption maximum in the frequency

\*\* For certain frequencies the computed absorption coefficient is smaller than the measured one by  $\sim 30 \pm 50\%$ .

The substitution in formula (4) of the structural Van Vleck-Weisskopf factor by the shape of the line from the kinetic equation [14], which appears to be currently the most correct, does not allow the bringing to agreement the theoretical and experimental data either [3] (see Figs 1-4).

It should, however, be noted that all the computed curves which were compared with the experimental results of [3], have been obtained without taking into account the nonresonance absorption of  $O_2$ . The neglecting of the latter by comparison with the resonance absorption in the region  $\nu = 48 \pm 70$  g.cps stems, according to authors of [3], from the estimate of the nonresonance part by the Debye formula and of the resonance part by that of Van Velck-Weisskopf. If instead of using the erroneous shape of the Van Vleck-Weisskopf line we utilized for the computation of the resonance part of  $O_2$  absorption the one according to the kinetic equation [14], the resonance part of absorption in the region  $\lambda \approx 5$  will vary very little [9]\*, since near the center of the line the various shapes are close to one another. As to the description of the nonresonance absorption by the Debye formula, the illegality of this was already more than once noted in literature [9, 13, 14, 19, 20]. In particular, measurements of atmosphere absorption in decimeter  $\lambda \approx 25 \pm 60$  cm [19, 31] and millimeter  $\lambda \approx 1 \pm 2$  mm waves [21], where radiowave damping in oxygen is conditioned only by the nonresonance part \*\*, are evidence that the Debye expression provides substantially underrated values for the nonresonance absorption coefficient  $\gamma_{np}$ .

The mechanism of nonresonance oxygen absorption is linked, as is well known, with excitation at collisions of diagonal matrix elements of the magnetic molecular moment [6]. The quantum-mechanics analogue of nonresonance absorption are the Zeeman transitions, for the M-splitting of triplet oxygen levels takes place in the intermolecular magnetic field at collisions, and the magnitude of that splitting varies in the course of the collision. The classical methods (analogous, for example, to [23]) are not applicable for the calculation of the nonresonance absorption of  $O_2$ . At first, the expression for  $\gamma_{np}$  was obtained by Stankevich [20] with the aid of the density matrix in specific idealizations. However, the extraction

\* Evidently,  $\nu_{K\pm}^0$  should be, first of all, substituted by  $\nu_{K\pm}^0 - (\Delta\nu_{K\pm})^2/\nu_{K\pm}^0$  in the form of the Van Vleck-Weisskopf line.

\*\* [see page 8]

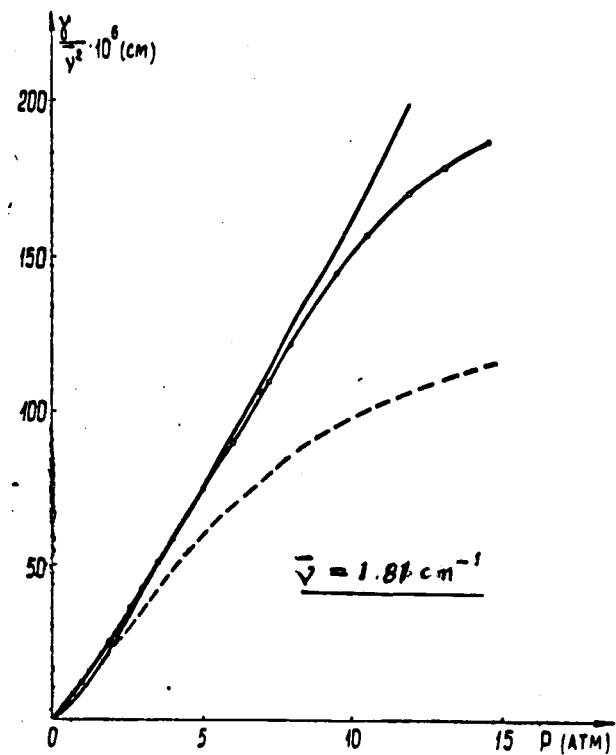


Fig. 1

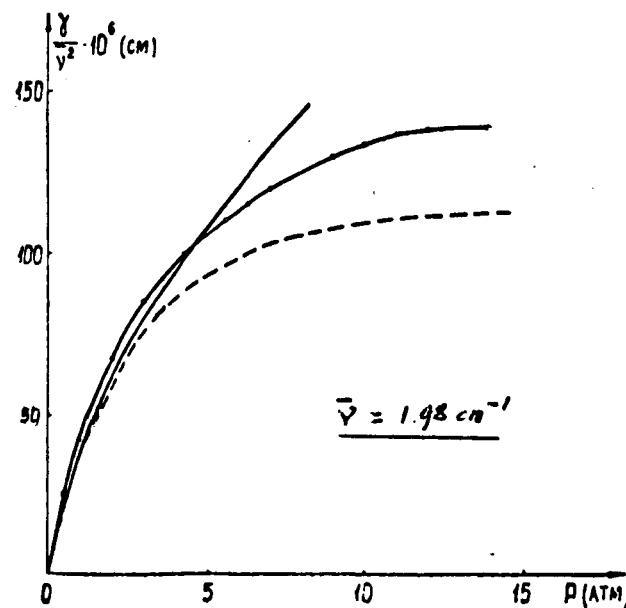


Fig. 2

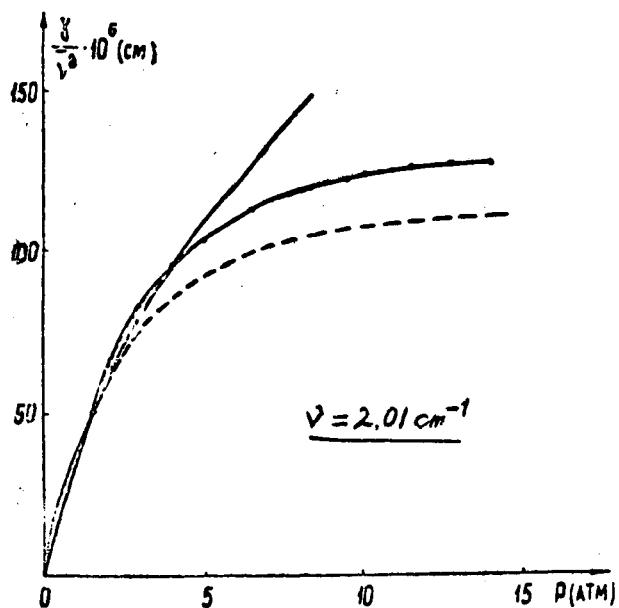


Fig. 3

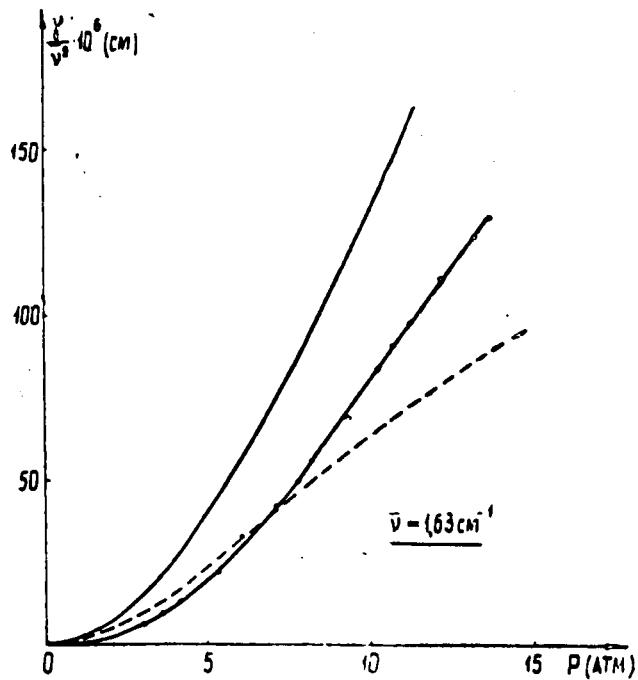


Fig. 4

\*\* [from page 6].. In a clear atmosphere radiowaves in the 25 - 60 cm band are absorbed only by oxygen molecules; at the same time, the resonance part of the absorption coefficient is much less than the nonresonance one (the corresponding ratio being near 0.01 %). In wavelengths  $\sim 1 - 2$  mm the absorption in the atmosphere under standard conditions is determined by the rotational spectrum of water vapors [22]. However, the oxygen part of absorp-

of quantitative information is in this case also beset with cumbersome calculatory procedures. No strict kinetic examination of the question of nonresonance absorption of  $O_2$  in the entire microwave band has been made available to date.

Meanwhile, the interpolation of experimental data [19, 21, 24, 25, 31] leads to the following empirical formula for the coefficient of nonresonance absorption of radiowaves by atmospheric oxygen at sea level in the band  $\nu = 40 \pm 100$  g. cps :

$$\gamma_{np}^0 [\delta\sigma/\kappa M] = 0,022 + 1,02 \cdot 10^{-3} (\nu - 40). \quad (5)$$

It may be seen from formula (23) of the work [20] that at binary molecular collisions the value of  $\gamma_{np}^0$  near the resonance frequencies is proportional to  $P^2$  (far from the resonance  $\gamma_{np}^0 \sim P^3$  [20]). Inasmuch as the excitation of the magnetic moment of  $O_2$  takes place in the magnetic field of the neighboring molecules, not all the molecular collisions by far are responsible for nonresonance absorption. Of all the main atmospheric gases only oxygen molecules are endowed with a magnetic dipole moment; that is why the collisions  $O_2 - O_2$  are capable of exciting the magnetic dipole moment, while the collisions  $O_2 - N_2$  are ineffective (at least in the dipole-dipole approximation for the value of the nonresonance absorption of oxygen). Taking into account the concentration of oxygen in the atmosphere  $f = 0.21$  and the circumstance that  $\gamma_{np} \sim f^2$ , we may write the formula (5) for pure oxygen in the form

$$\gamma_{np} [\delta\sigma/\kappa M] = [0,50 + 2,31 \cdot 10^{-2} (\nu - 40)] \left( \frac{P}{760} \right)^2. \quad (6)$$

In formula (6)  $\nu$  is expressed in g. cps and  $P$  in mm. Hg.

Evidently, the description of the nonresonance absorption of electromagnetic waves by oxygen molecules using the correlation (6) is quite rough. Formula (6) rather gives a smoothed (averaged) course of the value of  $\gamma_{np}$  by the band. However, the already hastily introduced calculations are evidence that the accounting for the nonresonance absorption may result sufficient for the interpretation of measurements of [3] up to pressures  $P \approx 7$  atm. In reality, the resonance absorption  $\gamma_p$  in the region  $\lambda \approx 5$  mm varies little

---

.. continued from page 8 ] .... tion in these waves is determined by the nonresonance absorption.

at pressures  $P \geq 6 + 7$  atm (see Figs. 1 - 3), while the nonresonance part of absorption  $\gamma_{np}$  rises proportionally to  $F^2$  (at binary collisions of molecules). Thus, at  $P \approx 1$  atm and in the frequency  $\nu = 1.98 \text{ cm}^{-1}$  the ratio is  $\gamma_{np}/\gamma_p \approx 1.7\%$ , and at  $P \approx 6$  atm, it is  $\gamma_{np}/\gamma_p \approx 24\%$ .

3. - We computed the absorption coefficient of molecular oxygen of 100% concentration on a computer using the formula

$$\gamma [\partial\delta/\kappa M] = APT^{-3}\nu^2 \sum_K (F_{K+}\mu_{K+}^2 + F_{K-}\mu_{K-}^2) e^{-BhcK(K+1)/kT} + \\ + [0.50 + 2.31 \cdot 10^{-2}(\nu - 40)] \left( \frac{P}{760} \right)^2, \quad (7)$$

where the nonresonance part of absorption is described by a semiempirical interpolation expression (see above), and the resonance part - analogously to [9]. In formula (7)  $A = 12.73^*$

$$F_{K\pm} = \frac{4\nu_{K\pm}^2 \Delta\nu_{K\pm}}{(\nu_{K\pm}^2 - \nu^2)^2 + 4\nu^2 (\Delta\nu_{K\pm})^2}, \quad \mu_{K+}^2 = \frac{K(2K+3)}{K+1}, \\ \mu_{K-}^2 = \frac{(K+1)(2K-1)}{K},$$

$P$  is expressed in mm. Hg,  $\nu$  in g. cps, the temperature  $T$  was assumed to be  $300^\circ\text{K}$ . The resonance frequencies using in calculations, were borrowed from [5] (see Table 1) \*\*. The resonance frequencies  $\nu_{K\pm}$  for the values  $K = 1 + 23$  were measured at low pressure in [26 - 29]. The measured values of  $\nu_{K\pm}$  coincide with the values computed in [28, 29] (discrepancy  $\lesssim 0.003\%$ ), which is evidence of sufficient precision of computed values  $\nu_{K\pm}$  even at  $K > 23$ , that is, for those transitions whose resonance frequencies were not measured. The half-widths of the spectral lines of  $O_2$  were computed by us according to formula  $\Delta\nu_{K\pm} = \delta\nu = (\alpha_{K\pm})_{cp} P$ , the value  $1.17 \text{ g. cps/mm Hg}$ , found in [9], being at the same time used for  $(\alpha_{K\pm})_{cp}$ . For  $P = 760 \text{ mm Hg}$  the indicated value of  $(\alpha_{K\pm})_{cp}$  in pure oxygen leads to  $\delta\nu \approx 0.030 \text{ cm}^{-1}$ , while in the atmosphere  $\delta\nu \approx 0.027 \text{ cm}^{-1}$ .

\* The coefficient  $A$  is greater than  $A_1$  of work [9] by  $1/0.21 = 4.76$  times, for in [9] oxygen in the atmosphere is being considered.

\*\* In the section 3 of this work we drop the index 0 in the denotation as we estimate that the resonance frequencies of  $O_2$  do not vary at pressures considered.

The absorption coefficient of molecular oxygen, computed by the formula (7) in units of  $\gamma \cdot 10^6/\nu^2$  at  $P = 0 \pm 14$  atm is compared in Fig. 1 - 4 (solid curve) with the experimental results of [3], marked by circles. The dashed curve represents the absorption coefficient of  $O_2$  computed with a line shape according to the kinetic equation and without taking into account the nonresonance part of absorption.

TABLE 1

RESONANCE FREQUENCIES OF  
MOLECULAR OXYGEN

Quantum number <i>K</i>	$\nu_{K+}$ [g.cps]	$\nu_{K-}$ [g.cps]
1	56,2652	118,7455
3	58,4466	62,4862
5	59,5910	60,3060
7	60,4348	59,1642
9	61,1506	58,3239
11	61,8002	57,6123
13	62,4112	56,9687
15	62,9978	56,3632
17	63,5685	55,7841
19	64,1276	55,2208
21	64,6789	54,6725
23	65,2241	54,1300
25	65,7616	53,5976
27	66,2978	53,0695
29	66,8313	52,5458
31	67,3627	52,0259
33	67,8923	51,5091
35	68,4205	50,9949
37	68,9478	50,4830
39	69,4741	49,9730
41	69,9998	49,4648
43	70,5249	48,9582
45	71,0497	48,4530
47	71,5743	47,9492
49	72,0986	47,4465

It may be seen from Figs 1 - 3 that in the frequencies  $\bar{\nu} = 1.8 \text{ cm}^{-1}$  ( $54.3 \text{ g.cps}$ ),  $1.98 \text{ cm}^{-1}$  ( $59.4 \text{ g.cps}$ ),  $2.01 \text{ cm}^{-1}$  ( $60.3 \text{ g.cps}$ ), the departure of the computed absorption coefficient using formula (7) from the measured one does not exceed 15% to pressures  $P \approx 7 - 8$  atm. In these frequencies the power corresponds to experiment theory no worse than in [3]; however, the description of the  $O_2$  spectrum in the given work is done, contrary to [3] without any additional hypotheses, which moreover call for serious doubts. (see section 1).

If alongside with the nonresonance absorption of  $O_2$  which undoubtedly takes place, we take into account the frequency shift  $\nu_{K\pm}$ , proposed by the authors of [1, 3], the departure between the experimental and theoretical results in the frequencies  $\bar{\nu} = 1.81 \text{ cm}^{-1}$ ,  $1.98 \text{ cm}^{-1}$  and  $2.01 \text{ cm}^{-1}$  at  $P \leq 7 \text{ atm}$  will reach  $30 \pm 40\%$ .

In two other frequencies  $\bar{\nu} = 1.63 \text{ cm}^{-1}$  (48.9 g. cps) and  $2.29 \text{ cm}^{-1}$  (68.7 g. cps), which belong to the ends of the investigated band ( $48 \pm 70$  g. cps) the agreement of our calculation with the data of [3] is worse than in the frequencies indicated above (see Fig. 4). This is explained apparently by the circumstance, whereby the correlation (6) is quite roughly describing the resonance absorption. Meanwhile, the details of nonresonance absorption acquire substantial significance at the ends of the band  $48 \pm 70$  g. cps, where the resonance and noresonance parts of absorption are already commensurate at standard conditions. It should however be noted that in the frequencies of  $1.63 \text{ cm}^{-1}$  and  $2.29 \text{ cm}^{-1}$ , a rough approximation of nonresonance absorption leads also to the overrating of experimental results. This allows us to hope for the effectiveness of the discussed absorption mechanism at its more precise description in these frequencies. The only exception is at  $\bar{\nu} = 1.89 \text{ cm}^{-1}$ , where the experimental results of [3] exceed both, our results and those computed in [3] for the value of the absorption coefficient of  $O_2$  with resonance frequencies shift.

Alongside with the approximate character of the description of nonresonance absorption within the framework of binary collisions model we should also point out that the binary collision model itself becomes invalid at high pressures. Thus, spectroscopical estimates, completed while taking into account the value of the effective diameter of molecule  $O_2$  collisions, show that at pressures  $P \approx 8 \pm 9 \text{ atm}$ , one should expect collisions between more than two molecules in oxygen. That is why the bad agreement between the calculated and experimental curves in Figs. 1 - 3 at  $P \geq 7 \div 8 \text{ atm}$  may be explained by the influence of numerous collisions and an increase of the role of details in the description of nonresonance absorption which are not accounted for in formula (6). Finally, the experimental material on radiowave absorption by oxygen molecules at increased pressure has, so far, a fragmental character, and not all the experimental data may be interrelated. Thus,

the measurements of [1] at  $P \approx 3 + 8$  atm in the frequency  $\nu = 2.3$  g. cps, where the absorption is determined only by the nonresonance part of the spectrum, agree satisfactorily with the computations by the Debye formula (discrepancy  $\leq 15\%$ ), though the latter, as already mentioned above, does not reflect at all the essence of nonresonance absorption of  $O_2$  and provides a correct order of magnitude of the absorption coefficient for molecular oxygen in certain wavelengths for a fixed pressure only on condition of successful assortment of the magnitude of the relaxation parameter. However, experimental data of [1] in the frequency  $\nu = 2.3$  g. cps appear to be substantially underrated by comparison with the measurements of ref. [19, 24, 31], if the latter are converted to pure oxygen at pressures  $P \approx 3 + 8$  atm.

Taking into account the results of the works [2, 3] and the annotations of the present work, we should conclude that the absorption spectrum of  $O_2$  in the band  $\nu = 48 - 70$  g.cps may be described by the standard method (see [9]) to pressures  $P \approx 7 + 8$  atm. At the same time, we have to estimate that the resonance frequencies of oxygen transitions are not dependent on pressure (see Table 1).

The author is indebted to S. A. Zhevakin for reading the manuscript and presenting his remarks, to K. S. Stankevich for the useful discussion and also to I. A. Rakova for her help in improving the results.

\*\*\* — THE END — \*\*\*

Contract No. NAS-5-376  
Consultants and Designers, Inc.  
Arlington, Virginia

Translated by ANDRE L. BRICHANT  
on 6 - 8 December 1965

R E F E R E N C E S

1. A. A. MARYOTT, J. BIRNBAUM. Phys. Rev., 99, 1886, 1955; J. Chem. Phys., 32, 686, 1960.
2. M. MIZUSHIMA. J. Chem. Phys. 32, 691, 1960.
3. A. BATTAGLIA, A. GOZZINI, M. IANNUZZI. Arc. sci., 14, fasc. spec., 93, 1961.
4. M. IANUZZI, N. MINNAJA. Nuovo Cimento, 39, 997, 1963.
5. A. H. BARRETT. Mémoires de la Société royale des Sciences de Liége, 7, fasc., unique, Liège Université, 1963.
6. J. H. VAN VLECK. Phys. Rev., 71, 413, 1947.
7. M. STRENDBERG. Radiospektroskopiya, IL, M., 1956.
8. M. TINKHAM, M. W. P. STRANDBERG. Phys. Rev., 97, 937, 1955; 99, 537, 1955.
9. S. A. ZHEVAKIN, A. P. NAUMOV. Radiotekhnika i elektronika, 10, 998, 1965.
10. J. O. ARTMAN, J. P. GORDON. Phys. Rev., 96, 1237, 1954.
11. L. F. STAFFORD, C. W. TOLBERT. J. Geoph. Res., 68, 3431, 1963.
12. J. H. VAN VLECK, V. E. WEISKOPF. Fev. Mod. Phys., 17, 227, 1945.
13. E. P. GROSS. Phys. Rev., 97, 395, 1955.
14. S. A. ZHEVAKIN, G. M. STRELKOV. Materialy XV Vsesoyuznogo soveshchaniya po spektroskopii, Minsk, 1963.
15. M. L. MEEKS. J. Geoph. Res., 66, 3749, 1961.
16. CH. TAUNS, A. SHAVLOV. Radiospektroskopiya, IL, M., 1959.
17. H. MARGENAU. Phys. Rev., 76, 1423, 1949.
18. P. W. ANDERSON. Phys. Rev., 75, 1450, 1949.
19. V. P. LASTOCHKIN, K. S. STANKEVICH. Izv. vyssh. uch. zav. ---Radiofizika, 6, 1098, 1963.
20. K. S. STANKEVICH. Izv. vyssh. uch. zav. ---Radiofizika, 8, 98, 1965.

21. M. COHN, F. L. WENTWORTH, J. C. WILTSE. Proc. IEEE, 51, 1227, 1963.
  22. S. A. ZHEVAKIN, A. P. NAUMOV. Radiotekhnika i elektronika, 9, 1327, 1964.
  23. A. A. MARYOTT, G. BIRNBAUM, J. Chem. Phys., 36, 2026, 1962.
  24. S. A. ZHEVAKIN, V. S. TROITSKIY, N. M. TSEYTLIN. Izv. vyssh. uch. zav. ---Radiofizika, 1, No. 2, 19, 1958.
  25. V. P. LASTOCHKIN, K. S. STANKEVICH, K. M. STREZHNEVA. Izv. vyssh. uch. zav. ---Radiofizika, 7, 984, 1964.
  26. J. H. BURKHALTER, R. S. ANDERSON, W. V. SMITH, W. GORDY. Phys. Rev., 79, 651, 1950.
  27. B. V. GOKHALE, M. W. P. STRANBERG. Phys. Rev., 84, 844, 1951.
  28. M. MIZUSHIMA, R. HILL. Phys. Rev., 93, 745, 1954.
  29. R. M. ZIMMERER, M. MIZUSHIMA. Phys. Rev., 121, 152, 1961.
  30. S. A. ZHEVAKIN, A. P. NAUMOV. Izv. vyssh. uch. zav. ---Radiofizika (v pechati).
  31. L. N. BONDAR', V. D. KROTIKOV, K. S. STANKEVICH, N. M. TSEYTLIN. Radiotekhnika i elektronika, 10, 755, 1965.
-

ST - AM - RWP - 10423 [17 pp. 80 cc]DISTRIBUTION

<u>GODDARD SPACE F.C.</u>	<u>NASA HQS</u>	<u>OTHER CENTERS</u>
100 CLARK, TOWNSEND	SS NEWELL, NAUGLE	<u>A R C</u>
110 STROUD	SG MITCHELL	SONETT [5]
400 BOURDEAU	SCHARDT	LIB. [3]
610 MEREDITH	SCHMERLING	
SEDDON	DUBIN	
611 McDONALD	SL LIDDEL	<u>LaRC</u>
ABRAHAM	FELLOWS	160 ADAMSON
BOLDT	EASTER	213 KATZOFF
VKB	HIPSHER	231 O'SULLIVAN
WILLIAMS	HOROWITZ	235 SEATON
612 HEPPNER	SM FOSTER	185 WEATHERWAX [2]
NESS	ALLENBY	
613 KUPPERIAN	GILL	<u>UCLA</u>
REED	BADGLEY	COLEMAN
614 WHITE	RR KURZWEG	<u>UC BERKELEY</u>
WOLFF	RTR NEILL	WILCOX
615 BAUER	ATSS SCHWIND	
AIKIN	ROBBINS	<u>U MICH.</u>
GOLDBERG	WX SWEET	ARNOLD
STONE		
WHIPPLE		<u>M I T</u>
620 SPENCER		BARRETT
NEWTON		<u>JPL</u>
NORDBERG		BARTH
TAYLOR		SNYDER, WYCKOFF
Brinton		<u>SWCAS</u>
BRACE		JOHNSON
SMITH		<u>WPAFB</u>
630 GI for SS [5]		Code TDBX-T
640 H E S S [3]		
641 MAEDA		
HARRIS		
BURLEY		
252 LIBRARY		
256 FREAS		